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ESR study of the radical polymerization of styrene 6

ESR spectra of propagating radicals from deuterated styrenes

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Summary

To assign definitely the hyperfine coupling constants for the α- and β-protons of the well-resolved spectrum of poly(styrene) radical, five types of deuterated styrenes were synthesized and polymerized in the cavity of an ESR spectrometer. Their propagating radicals which presented sufficiently high concentrations were subjected for ESR measurement during polymerization in bulk. The spectra obtained exhibited different splitting patterns depending on the number and positions of deuteration. The relevant hyperfine coupling constants for the protons and deuteriums bound to the respective terminal units of the propagating radicals were determined. As a result, the coupling constants for the α- and β-protons of the poly(styrene) radical, a_α = 15.90 G, and a_β = 18.30 and 15.90 G, were unambiguously confirmed.

Introduction

It was thought that propagating radical of free radical polymerization in a homogeneous system could not be observed by ESR spectroscopy except for the spectra recorded by Bresler et al.[1] and Kamachi et al.[2] using a specially designed spectrometer and the cavity, respectively, because of extremely low concentration at the steady state. However, we have shown that the propagating radical of styrene (St) can be quantified by ESR spectroscopy during bulk polymerization after search of the optimum conditions of the polymerization and ESR measurement.[3] Quantification of the propagating radical by ESR spectroscopy does not require the steady state assumption; the absolute rate constants of propagation and termination of the St polymerization have been determined straightforwardly over wide conversion and temperature ranges.[4] The propagation rate constant has been confirmed to remain constant regardless of the chain length of the polymer radical.[5] Shen et al.[6] have also determined the propagation rate constants for the St polymerization by the ESR method at different conversions and temperatures.

Another type of important information afforded by ESR spectroscopy of propagating radical seems to be the resonance situation and conformation with respect to the radical center. We have also succeeded in recording the well-resolved spectrum of the poly(St) radical.[7,8] The observed spectrum of the poly(St) radical apparently consisting of more than twenty lines allowed evaluation of the hyperfine coupling constants (hfc's) for the

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α-, β-, *m*-, *o*-, and *p*-protons. The well-resolved spectrum of the polymer radical from *p*-methoxystyrene (*p*-MeO-St) was also recorded and the hfc's of all the protons including the methoxy protons were obtained.7)

The hfc's revealed that the unpaired electron is delocalized over the aromatic ring and that the resonance effect of the *p*-substituent bound to the conjugated system was observed as smaller hfc's for the α- and β-protons of the poly(*p*-MeO-St) radical. Anticipating a greater hfc for the α-proton of the poly(St) radical than that for the same proton of the poly(*p*-MeO-St) radical, we tentatively adopted a_α = 18.30 G and a_β = 15.90 G for the poly(St) radical in our previous communications.7,8) The hfc's assigned to the α and β-protons were greater than those assigned to the *m*-, *o*-, and *p*-protons, and the spectrum of the poly(St) radical was accounted for by a doublet (a = 18.30 G) of a triplet (a = 15.90 G) further split by the *m*-, *o*-, and *p*-protons.

However, there are two possible combinations of the hfc's for the α- and β-protons: 1) a_α = 18.30 G, $a_{\beta1}$ = 15.90 G, and $a_{\beta2}$ = 15.90 G, and 2) a_α = 15.90 G, $a_{\beta1}$ = 15.90 G, and $a_{\beta2}$ = 18.90 G. A similar situation with respect to the a_α and a_β values was also encountered in the spectrum of the poly(*p*-MeO-St) radical. In the case of 1), the a_α is greater than those for the benzyl and phenethyl radicals by ca. 2 G.9) Furthermore, the a_β tentatively assigned to the polymer radicals is less than that of the phenethyl radical.9) Although a greater a_β than a_α seems to be acceptable, both 18.30 and 15.90 G are not in agreement with the a_α and a_β for the phenethyl radical. No experimental confirmation has been available so far, and these uncertainties in the assignment of the hfc's have remained.

Mao et al.10) have recently recorded a 12-line spectrum consisting of rather broad lines. They have proposed based on simulation that the poly(St) radical is present in two conformations of which the hfc for the α- and β-protons are a_α =19.5, $a_{\beta1}$ = $a_{\beta2}$ = 15.8 G for a 6-line spectrum, and a_α = 13.8-15.8, $a_{\beta1}$ = 35.5, and $a_{\beta2}$ = 9.5 G for an 8-line spectrum. However, the simulation was carried out using the hfc's for α- and two β-protons, and the hfc's for the protons bound to the aromatic ring of the St unit were not taken into account.

More recently, Kamachi and Kajiwara11) have recorded the well-resolved spectrum of the poly(St) radical by a single scan, determining the radical concentration for kinetic study. Furthermore, the spectra of the polymer radicals from 1,3-butadiene and substituted 1,3-butadienes,12) and those from methacrylic esters13) have been recorded. Narrow line-width of these spectra allows precise determination of the hfc's, and delocalization of the unpaired electron of the diene radicals and conformation of the methacrylate radical have been discussed in detail. ESR spectroscopy has become one of the most powerful tool for studying of radical polymerization.

For further study of St polymerization by the ESR method, the definite values of the a_α and a_β for the poly(St) radical have to be obtained. In the present work, we synthesized deuterated St's and measured the ESR spectra of their polymer radicals. Coupling with deuterium is ca. 1/6.5 of that with a proton,14) and the deuterium substitution of St may bring about significant changes in the splitting pattern of the spectrum of the poly(St) radical depending on the number and position of the deuteration. The hfc's for the α- and β-protons of the poly(St) and poly(*p*-MeO-St) radicals could be assigned on the basis of the spectral change arising from the deuteration.

Experimental

p-Deuteriostyrene (St-*p*-*d*), α-deuteriostyrene (St-α-*d*), 2,3,4,5,6-pentadeuteriostyrene (St-d_5), α,2,3,4,5,6-hexadeuteriostyrene (St-d_6), and β,β,2,3,4,5,6-heptadeuteriostyrene (St-d_7) were prepared by the sequence of reactions as follows.

$$p\text{-BrC}_6\text{H}_4\text{Br} \xrightarrow[\text{2) D}_2\text{O}]{\text{1) Mg}} p\text{-BrC}_6\text{H}_4\text{D} \xrightarrow[\text{2) CH}_3\text{CHO}]{\text{1) Mg}} \text{CH}_3\text{CH(OH)C}_6\text{H}_5\text{D-}p \xrightarrow[\Delta]{\text{KHSO}_4}$$

$$\text{CH}_2\text{=CHC}_6\text{H}_4\text{D-}p \quad \textbf{(St-}\boldsymbol{p}\textbf{-}\boldsymbol{d}\textbf{)}$$

$$\text{CH}_2\text{=CBr-C}_6\text{H}_5 \xrightarrow[\text{2) D}_2\text{O}]{\text{1) Mg}} \text{CH}_2\text{=CDC}_6\text{H}_5 \quad \textbf{(St-}\boldsymbol{\alpha}\textbf{-}\boldsymbol{d}\textbf{)}$$

$$\text{C}_6\text{D}_6 \xrightarrow{\text{Br}_2\text{/Fe}} \text{C}_6\text{D}_5\text{Br} \xrightarrow[\text{2) CH}_3\text{CHO}]{\text{1) Mg}} \text{CH}_3\text{CH(OH)C}_6\text{D}_5 \xrightarrow[\Delta]{\text{KHSO}_4}$$

$$\text{CH}_2\text{=CHC}_6\text{D}_5 \quad \textbf{(St-}\boldsymbol{d}_5\textbf{)}$$

$$\text{C}_6\text{D}_6 \xrightarrow{\text{(CH}_3\text{CO)}_2\text{O/AlCl}_3} \text{CH}_3\text{C(O)C}_6\text{D}_5 \xrightarrow{\text{LiAlD}_4} \text{CH}_3\text{CD(OH)C}_6\text{D}_5 \xrightarrow[\Delta]{\text{KHSO}_4}$$

$$\text{CH}_2\text{=CDC}_6\text{D}_5 \quad \textbf{(St-}\boldsymbol{d}_6\textbf{)}$$

$$\text{C}_6\text{D}_6 \xrightarrow{\text{(CH}_3\text{CO)}_2\text{O/AlCl}_3} \text{CH}_3\text{C(O)C}_6\text{D}_5 \xrightarrow{\text{D}_2\text{O/K}_2\text{CO}_3} \text{CD}_3\text{C(O)C}_6\text{D}_5 \xrightarrow{\text{LiAlH}_4}$$

$$\text{CD}_3\text{C(OH)C}_6\text{D}_5 \xrightarrow[\Delta]{\text{KHSO}_4} \text{CD}_2\text{=CHC}_6\text{D}_5 \quad \textbf{(St-}\boldsymbol{d}_7\textbf{)}$$

Structures of the deuterated St's were verified by ^{1}H-NMR spectroscopy after repeated distillation under reduced pressure. Extent of deuterium substitution of all the monomers synthesized was determined by ^{1}H-NMR spectroscopy. *tert*-Butyl peroxide (TBP) was distilled under reduced pressure. Methyl 2,2'-azobisisobutyrate (MAIB) was commercially available and purified by recrystallization from n-hexane.

ESR spectra were taken by a Bruker ESR 300 spectrometer at X band with 100 KHz field modulation using a quartz tube of 5 mm o.d. The polymerization was initiated with TBP or MAIB as a photosensitizer under irradiation of a 500 W xenon lamp at room temperature. Computer simulation of the spectra was performed by a program based on the procedure originally reported by Maki and Stone.15) ^{1}H-NMR spectra were recorded on a JEOL α-400 spectrometer. Deuteriochloroform and tetramethylsilane were used as the solvent and the internal standard, respectively.

Results and discussion

Spectra of propagating radicals of deuterated monomers

The extent of the deuteration of the synthesized monomers is summarized in Table 1, predicting that the spectra of the deuterated radical can be obtained. The polymerizations of the deuterated St's were sensitized with TBP or MAIB at room temperature. Replace-

Table 1. Extent of deuteration

Monomer	Extent of deuteration (%)		Monomer	Extent of deuteration (%)	
	Vinyl group	Aromatic group		Vinyl group	Aromatic group
St-α-*d*	95.1	-	St-d_6	99.6	97.7
St-*p*-*d*	-	80.6			
St-d_5	-	99.0	St-d_7	94.6	98.1

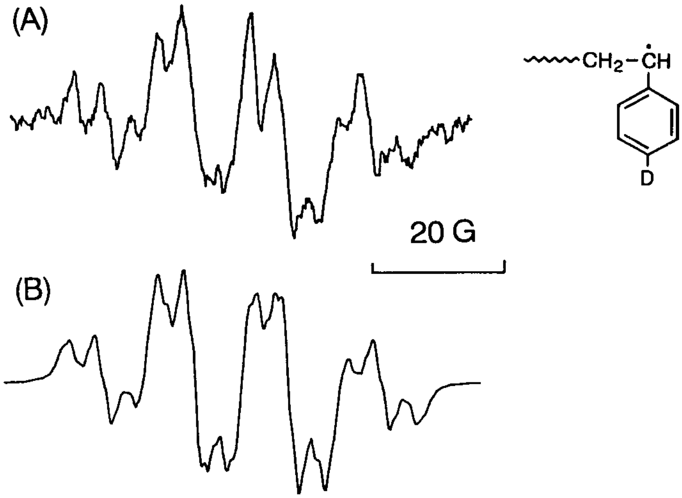

Fig. 1. ESR spectrum of poly(St-*p*-*d*) radical recorded during bulk polymerization sensitized with TBP (0.8 mol/L) by UV irradiation at room temperature after accumulation of 67 scans (A) and a simulated spectrum for A (B)

ment of a proton with a deuterium at a specific position of the St unit results in a change in splitting into a doublet to a 1 : 1 : 1 triplet by a hfc of ca . $a_H/6.5$.[14] Consistently, splitting patterns of the spectra were varied significantly as the number and position of the deuteration. Fig. 1 shows the ESR spectrum observed in the polymerization of St-*p*-*d*, and the computer simulation for the spectrum of the deuterated radical. The hfc's determined are summarized in Table 2.

The hfc's obtained confirm the magnitude of the hfc's for three types of the protons, the α-, β-, and β-protons, already reported for the poly(St) radical. The hfc for the *p*-deuterium was estimated to be 0.9 G, whereas the magnitude of this value which only contributes to increase in line width does not affect the splitting pattern. The simulation for the spectrum of the poly(St-*p*-*d*) radical in Fig. 1 could not offer any decisive information whether a = 18.3 or 15.9 G should be assigned to the α-proton.

Table 2. Comparison of hfc's for polymer radicals from St and deuterated St with those of low molecular weight radicals

Polymer radical	Hfc (G)				
	a_α	a_β	a_m	a_o	a_p
St-*p*-*d*	15.8	15.8, 18.1	1.6	4.9	0.9[a]
St-α-*d*	2.6[b]	15.5, 18.1	1.8	5.0	5.9
St-d_5	15.7	15.7, 18.3	0.82	0.7	0.9
St-d_6	n.d.	33.5[c]	n.d.	n.d.	n.d.
St-d_7[d]	15.2	n.d.	n.d.	n.d.	n.d.
St[e]	15.90	15.90, 18.30	1.70	4.95	5.95
p-MeO-St[e]	15.50	15.50, 17.70	1.20	4.80	0.30
Benzyl[g]	16.25	-	1.70	5.10	6.13
Phenethyl[g]	16.25	17.69	1.65	4.95	5.90
Cummyl[g]	-	16.30	1.65	4.70	5.55

a) Hfc for *p*-deuterium. b) Hfc for α-deuterium. c) ($a_{\beta1}$ + $a_{\beta2}$). d) Hfc's for deuteriums in β-, *m*-, *o*-, and *p*-positions were not determined definitely because of broad line width. e) Ref. 7. f) Hfc from the methoxy protons. g) Ref. 9.

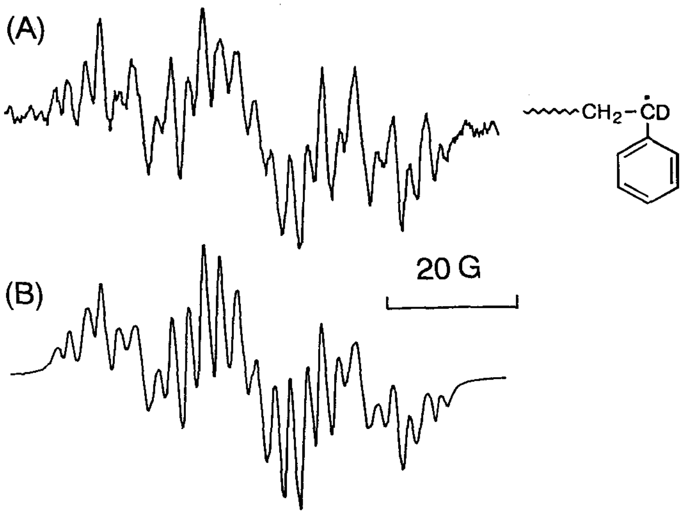

Fig. 2. ESR spectrum of poly(St-α-*d*) radical observed during bulk polymerization sensitized with TBP (0.8 mol/L) by UV irradiation at room temperature after accumulation of 86 scans (A) and a simulated spectrum for A (B)

In the case of the the poly(St-α-*d*) radical, the spectrum in Fig. 2 consists of relatively narrow lines. The computer simulation required two types of hfc's greater than 15 G. The hfc of the α-deuterium could not be greater than 3 G, and the a_α is estimated to be

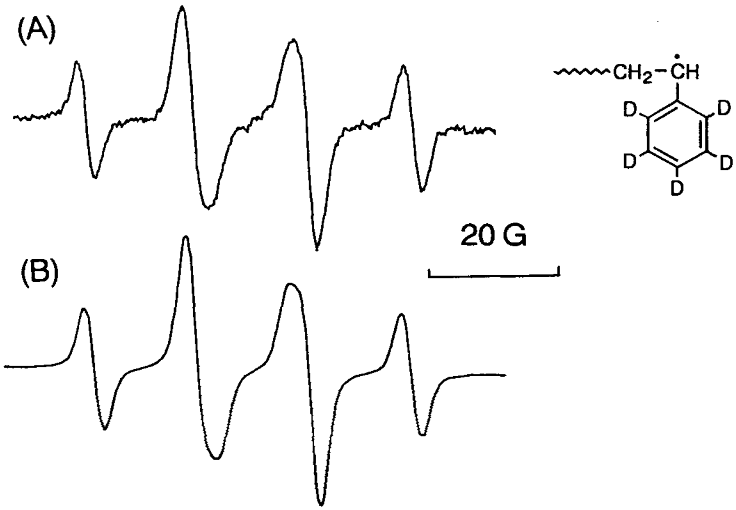

Fig. 3. ESR spectrum of poly(St-d_5) radical observed during bulk polymerization sensitized with TBP (0.8 mol/L) by UV irradiation at room temperature after accumulation 23 scans (A) and a simulated spectrum for A (B)

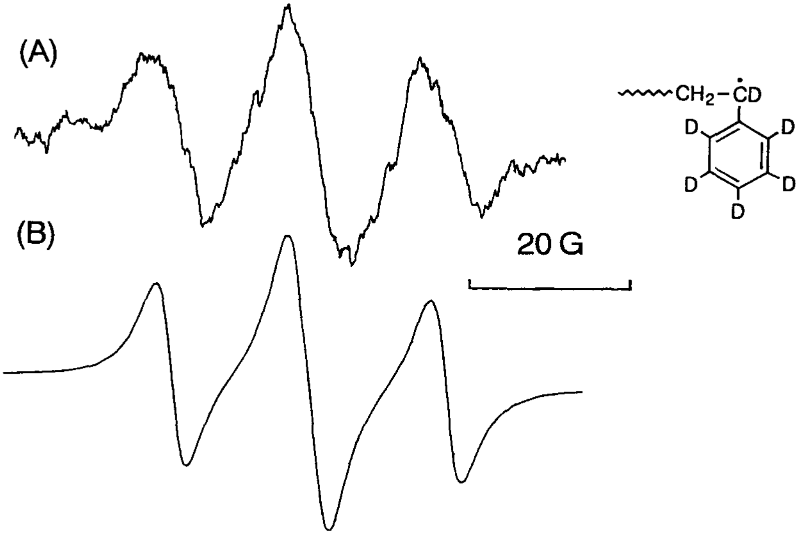

Fig. 4. ESR spectrum of poly(St-d_6) radical observed during bulk polymerization sensitized with MAIB (0.18 mol/L) by UV irradiation at room temperature after accumulation of 5 scans (A) and a simulated spectrum for A (B)

15.9 or 18. 3 G. Different hfc's are assigned to the β-protons. Almost the same spectrum of the poly(St-α-*d*) radical was recorded irrespective of temperature up to 100°C, and two values for the β-protons were confirmed. Two values for a_β seem to be inherent not only to the poly(St-α-*d*) radical but also to the poly(St) radical.

Smaller hfc's for all the protons bound to the phenyl group of the poly(St) radical than those for the α- and β-protons decreased further in the spectrum of the poly(St-d_5) radical leading to a 4-line spectrum broadened significantly as shown in Fig. 3. Two values of the hfc for the α- and β-protons were unambiguously determined from the line spacing and confirmed by the simulation. The splitting due to the *m*-, *o*-, and *p*-deuteriums were not estimated from the line spacings, and the coupling with these collapsed to broaden the lines. The hfc's determined are given in Table 2.

It should be noted that the poly(St-d_5) radical yields a broad 4-line spectrum of much better signal to noise ratio than that of the poly(St) radical, because the coupling with the deuterium bound to the aromatic ring is too small to form separated lines as shown in Table 2. As a result, St-d_5 may be used instead of St for more precise quantification of the polymer radical.

For further confirmation of the magnitude of the hfc's for the α- and β-protons, the spectra of the ply(St-d_6) and poly(St-d_7) radicals were measured. MAIB was used as the photosensitizer instead of TBP for the polymerization of St-d_6 and St-d_7 polymerization in the cavity. However, the radical species detected are sufficiently high molecular weight, and type of initiator should not influence on the spectra of the propagating radicals. The poly(St-d_6) radical yielded a 3-line spectrum as shown in Fig. 4. Because of rather broad

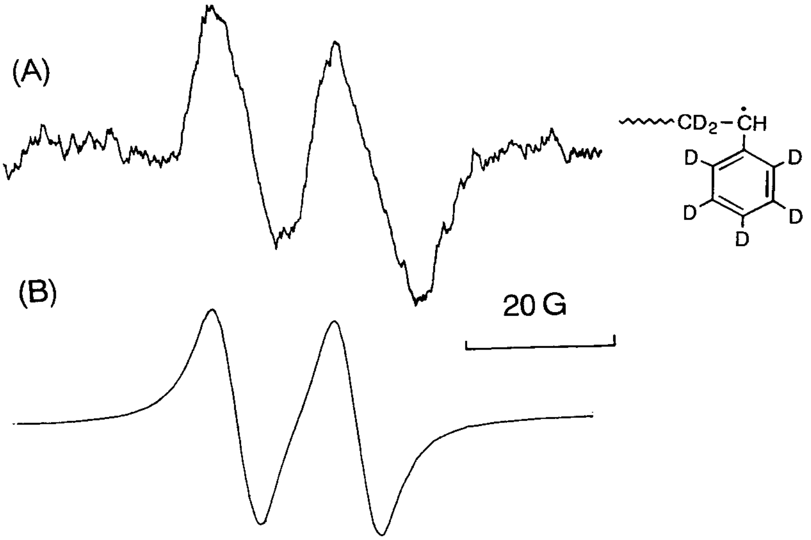

Fig. 5. ESR spectrum of poly(St-d_7) radical observed during bulk polymerization sensitized with MAIB (0.19 mol/L) by UV irradiation at room temperature after accumulation of 10 scans (A) and a simulated spectrum for A (B)

line width, the summation of the hfc's for the two β-protons was obtained from the line spacing between the outermost lines: $a_{\beta 1} + a_{\beta 2} = 33.5$ G. The summation of the a_β values is apparently greater than twice of 15.90 G and this consequence confirms the assignment of the different hfc's for two of the β-protons.

The radical of St-d_7 bears only one proton in the α-position. The hfc for the α-proton is expected to be significantly larger than those for the deuteriums bound to the remaining positions of the monomeric unit leading to unambiguous assignment of the a_α value. A doublet spectrum shown in Fig. 5 was obtained, and the a_α was evaluated from the line spacing, $a_\alpha = 15.2$ G. Considering the assignment of the deuterated radicals and the St-d_7 radicals, we can conclude that the hfc's for the α- and β-protons bound to the St unit carrying an unpaired electron are 15.90 G, and 15.90 and 18.30 G, respectively, as shown in Table 2. The hfc's for the poly(*p*-MeO-St) radical are also assigned as given in Table 2, $a_\alpha = 15.50$ G, and $a_\beta = 15.50$ and 17.70 G. According to the hfc's for all the protons of the poly(St) radical, significant spin densities on the aromatic carbons are predicted. Furthermore, non-equivalency of the β-protons evidences that the C_α-C_β bond of the St unit does not rotate freely.

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